

# PROMISING DIFFUSION BARRIER COATINGS FOR FLEXIBLE BACKAGING BASED ON FCVA TETRAHEDRAL AMORPHOUS CARBON FILMS

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## Abstract

In this study, surface modification of poly (ethylene terephthalate) (PET) polymeric substrates using Si-incorporated hydrogenated tetrahedral amorphous carbon (ta-C:Si:H) thin films deposited by filtered cathodic vacuum arc (FCVA) system under tetramethylsilane ( $\text{Si}(\text{CH}_3)_4$  (TMS) atmosphere has been investigated. A number of characterization techniques such as high-resolution synchrotron-based x-ray reflectometry, XRR, x-ray photoemission spectroscopy, XPS, multi-wavelength Raman spectroscopies, spectroscopic ellipsometry, SE, and surface profiler have been employed to investigate the role of microstructure, composition and surface morphology on the gas barrier performance of the FCVA films. We have demonstrated that 21 at.% of silicon-incorporation into the ta-C films has caused a complete reduction of the films' intrinsic-stress (i.e. 10 GPa) and a complete disappearance of the surface micro-cracks. Stress reduction was attributed to the development of weak Si-C bonds (3.21 eV) as revealed by XPS, which played a role in releasing bond distortion of the nearby strong  $\text{sp}^3$  C-C bonds (3.7 eV; 411  $\text{KJmol}^{-1}$ ). On the other hand, Si-addition significantly improved the permeation barrier performance against water vapor with a reduction factor up to 93%. In comparison with silicon-incorporated PECVD films [1] the results demonstrate that higher silicon- addition was needed for relaxing the highly stressed structure of ta-C films [10GPa]. In contrast to FCVA ta-C films, a thickness-dependence permeation study revealed that that solubility-diffusion was the main mechanism responsible for the transport of water vapor through ta-C:Si:H film/polymer composite.

## INTRODUCTION

Amorphous diamond-like carbon (DLC) is becoming a new focus in the research field of flexible electronics. In addition to good impermeability to water vapor and oxygen, which is necessary for such applications, DLC's possess intrinsic flexibility, high hardness, excellent chemical and thermal stability and they are transparent in the visible spectrum. However, high-level of intrinsic-stress (especially in the un-hydrogenated form of DLC) is a major drawback of these types of coatings. We have reported earlier that highly dense ta-C thin films with density ( $3.3 \text{ g/cm}^3$ ) near to that of diamond ( $3.5 \text{ g/cm}^3$ ) have shown unexpected high water vapor transmission rate (WVTR) ( $1.3 \text{ g/m}^3$ ) with gas reduction factor (RF) value of 17%. This is due to the release of high residual-stress, which has affected the surface morphology with a network of deep micro-cracks. The build up of such high-level of residual stress is thought to be an intrinsic property of these films caused by the subplantation process responsible on the growth of such hard films. Moreover, the transport of water vapor through surface inhomogeneties (i.e. micro-cracks) is responsible on permeation of water vapor through ta-C films/PET composite, which has resulted in poor gas barrier performance for these hard coatings [1]. However, Si-incorporated PECVD a-C:H stress-free films with lower density have shown high gas barrier performance with WVTR value of  $0.03 \text{ g/m}^3$  with RF value of 98%.

In this study, we employed the Si-addition strategy for releasing the residual-stress in hard FCVA ta-C thin coatings deposited at varying tetramethylsilane ( $\text{Si}(\text{CH}_3)_4$  (TMS) partial pressure onto PET polymeric substrates in an attempt to enhance the gas barrier performance of PET polymeric substrates.

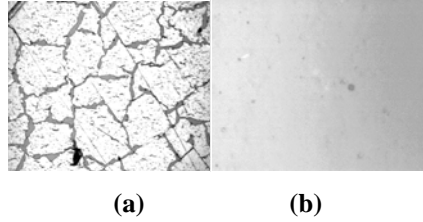
## Results and discussion

Figure 1.a displays an optical microscopy picture of PET polymer substrate coated with 130-nm-thick ta-C film where a network of cracks (wrinkles) spreads out over the whole substrate surface. AFM has revealed that these cracks have depths comparable to the film-thickness reaching down to the film/polymer interface. A similar surface morphology has been exhibited by a-C:H films on PET [1]. It is strongly believed that such a surface morphology should be attributed to the release of the residual-stress (9-13 GPa). To support the suggestion that residual-stress is the main reason for the observed surface morphology covered by a network of cracks, a series of ta-C films

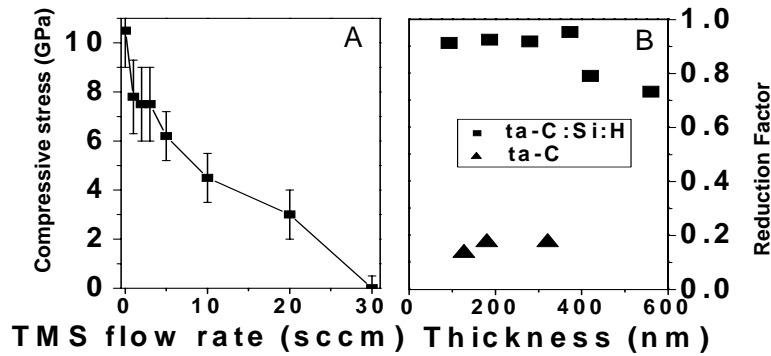
deposited at different TMS partial pressures ( $8.0 \times 10^{-7}$ - $1.0 \times 10^{-3}$ ) has been investigated for surface morphology. For films deposited at TMS flow rate of 40 sccm (21.5 Si at.%), a new structure has been observed that has almost zero compressive stress as indicated by surface-profilometric measurements. We have to emphasize that since TMS precursor gas has been used as a source of silicon, the new structure will include also hydrogen as well as silicon. Fig.1.b. shows an optical microscope image of 300-nm layer of ta-C:Si:H film on PET substrate. As one can see, the new surface morphology is completely free of any relevant relaxation (i.e. cracks).

Fig.2. illustrates the evolution of the residual stress of the FCVA ta-C films deposited under varying TMS partial pressure on Si substrates. As one can see, the compressive stress exhibited a progressive reduction from  $\sim 10.5$  GPa at 0.5 at.% silicon to almost 0 GPa with the increase in Si concentration up to 21.5 at.%. Since the bond strength of Si-C ( $320 \text{ KJ mol}^{-1}$ ) is smaller than that of the  $\text{sp}^3$ -hybridized C-C bonds ( $411 \text{ KJ mol}^{-1}$ ), the formation of Si-C could be responsible for the reduction in residual stress in Si-incorporated films [2]. The high level of hydrogen may have prevented SiC crystallite formation by terminating ‘dangling bonds’ during the film growth process, especially for films with high Si/C ratios [3]. Moreover, Si-H bonds may also participate in causing the relaxation of the three-dimensional rigid network of ta-C:Si:H structure and reduce the film stress.

The induced structural modification caused by si-addition with stress-relief has led to not only the enhancement in the surface morphology but also significantly improved the gas barrier performance of ta-C:Si:H films in comparison with ta-C films ( as presented in the inset of Fig.2). The reduction in water vapor reached a value of 93 % for 400 nm-thick- ta-C:Si:H films. As a conclusion, this work demonstrated the feasibility of using modified ta-C films on soft substrates that could open a new application window for such a promising material.



**Figure 1.** Optical microscopy pictures of a PET substrate (magnification of X10) coated with (a) ta-C film and (b) ta-C:Si:H film. The figure clearly illustrates the effect of Si- and hydrogen-addition on the surface morphology of PET coated substrate.



**Figure 2.** (a) Compressive residual stress (evaluated by stylus profiler) of ta-C:Si:H films deposited on Si substrate at different TMS partial pressure (flow rate). (b) The reduction factor, RF, of water vapor permeation through the ta-C and Si-a:C:H coated-PET as a function of coating thickness ( $\text{WVTR}_{\text{PET}}: 1.968 \text{ g/m}^2 \text{ day}$ ).

## REFERENCES

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